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de Wijs, G.A.; de Groot, R A

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Towards 100% spin-polarized charge-injection: The half-metallic NiMnSb/CdS interface

G. A. de Wijs[1] and R. A. de Groot[1,2]
[1]*Electronic Structure of Materials, Research Institute for Materials, Faculty of Sciences, Toernooiveld 1, NL-6525 ED Nijmegen, The Netherlands*
[2]*Laboratory of Chemical Physics, Materials Science Center, Rijksuniversiteit Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands*
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Spin-electronics requires an electron source with a spin-polarization as high as possible. For this, half-metallic materials seem ideally suited as they exhibit 100% spin polarization. Because of its high Curie temperature and compatibility with existing semiconductor technology, NiMnSb is a most desirable half metal. However, using first-principles calculations we find that NiMnSb surfaces are not half metallic, even if they are stoichiometric and perfectly ordered. Moreover, several surface and interface sensitive experiments have reported polarizations far less than 100%. These findings are easily rationalized, as they result from the symmetry breaking at the surface. We show that it is possible to restore half metallicity at interfaces, by a proper engineering at the microscopic level. Therefore the half metal NiMnSb is, in principle, a suitable source material for 100% spin-polarized charge carriers.

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The rapidly developing field of spin-electronics holds much promise for the future. Widely known possible applications are in nonvolatile magnetic random access memories, but also an increase of the efficiency of optoelectronic devices and even a self-assembled quantum computer[1] are envisaged. Key ingredient is a source of spin-polarized charge carriers. Conventional ferromagnetic metals are unsuitable source materials as the spin polarization P of the carriers injected into a semiconductor is negligible.[2] With magnetic semiconductors a high spin polarization of the injected charge carriers has been demonstrated.[3] These, however, are not spontaneous magnets and therefore require bias fields, a requirement which interferes with several applications. A natural choice for a polarized charge-carrier source are half-metallic systems. In these one spin direction behaves like a metal whereas, for the other, the Fermi level is in a gap. Thus they have $P=100\%$ as an intrinsic property.[4]

Half-metallic ferromagnets were discovered by theory with the prediction of 100% spin polarization for NiMnSb.[5] Since then others have been found, such as CrO_2,[6,7] the CMR (colossal magnetoresistance) doped manganites[7–10] and the CMR double perovskite Sr_2FeMoO_6.[11] Of these NiMnSb is particularly interesting because of its high Curie temperature ($T_C=760$ K) (Ref. 12) and its compatibility with existing semiconductor technology.

Much experimental effort is being devoted to NiMnSb (Refs. 13 and 14) but nevertheless highly spin-polarized carrier injection from NiMnSb has not yet been achieved. In fact, spin-polarized photoemission,[15] spin-polarized tunneling,[13] and Andreev reflection measurement[7] report values of P far below 100%. In contrast, many other experiments, such as spin-resolved positron annihilation[16] and infrared reflectance spectroscopy,[17] support the half-metallic nature of NiMnSb. Neutron diffraction gives a magnetic moment of $4.0(2)\mu_B$ (Ref. 12) and the resistivity does not exhibit the low-temperature T^2 dependence characteristic for spin-flip scattering.[18] The striking difference between these sets of experiments is that the latter probe the NiMnSb bulk, whereas the former are all, to some extent, surface or interface sensitive.

In this paper we report first-principles calculations on NiMnSb surfaces and interfaces. In contrast to the bulk, we find that NiMnSb surfaces and interfaces are not half metallic in general. We also show that for a *suitably chosen* NiMnSb/CdS interface half-metallicity can be restored throughout the entire interface region.

Electronic structures were calculated using density-functional theory in the generalized gradient approximation according to Ref. 19. Structural optimizations were carried out with the resulting Hellmann-Feynman forces.[20] Electron-ion interactions were described using ultrasoft pseudopotentials,[21,22] except in some calculations where we used the projector augmented-wave (PAW) method[23,24] for Mn instead. Calculations were carried out with the first-principles molecular-dynamics program VASP (Vienna *ab initio* simulation program).[25–27]

The crystal structure of NiMnSb is fcc ($F\bar{4}3m$), with Ni at (0,0,0), Mn at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and Sb at $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$. The site at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is empty. The Mn and Sb atoms are tetrahedrally surrounded by Ni atoms. Thus their local environment is similar to that in a zincblende semiconductor. Surfaces (interfaces) were modeled in a periodically repeated supercell, containing alternating slabs of NiMnSb and vacuum (insulator barrier material).

First we consider NiMnSb surfaces. We carried out calculations on several stoichiometric (100) and (111) surfaces. As an example, we discuss the surfaces of a (111) slab in more detail. We employed a hexagonal cell, with a and b fixed by the lattice constant of NiMnSb ($a=b=4.18$ Å, $\alpha=\beta=90°$, $\gamma=120°$). The bulklike stacking of the (111) slab along [111] is an Mn layer, a Ni layer, an Sb layer, and an empty layer (the layers are approximately 0.8 Å apart). The cell contains six formula units of NiMnSb, i.e., a slab of 23 atomic layers with a thickness of ~ 18.7 Å, and a vacuum

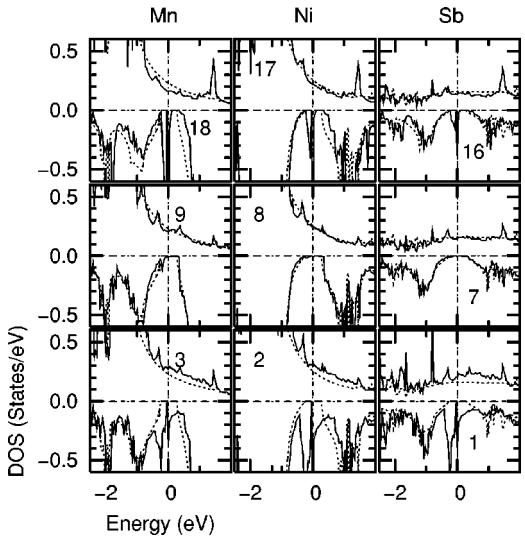

FIG. 1. Atom projected density of states near the Fermi level of the NiMnSb (111) slab with surfaces. The figure only depicts the projected DOS of layers near the surfaces and the slab center. The Fermi level is at 0. The majority and minority spin DOS are on the positive and negative ordinate, respectively. For reference, the bulk partial DOS are shown (dotted lines). The DOS has been calculated with the PAW method for Mn.

region of 8.6 Å. The two surfaces are (necessarily) inequivalent: On surface I the outer layer is antimony (Sb^1), on surface II it is manganese (Mn^{18}). The superscripts at the chemical elements count the occupied layers in the [111] direction, starting at surface I. Atomic positions have been optimized along [111].

Figure 1 shows the projected densities of states (DOS') of the layers at the surfaces and near the slab center. For the DOS calculation a $13\times13\times1$ **k**-point mesh[28] and tetrahedron interpolation were used.[29] Notice that in the central part of the slab (Sb^7-Mn^9) the bulk DOS is well reproduced, in particular the half metallic character is evident as the minority DOS vanishes at the Fermi level. Conversely surface states are present on both surfaces. They clearly show up in the minority spin component DOS at the Fermi level and spoil the half metallicity.

Also for (100) both possible bulk-terminated surfaces (one terminated with a MnSb layer and the other with a Ni layer) are not half metallic. We obtain the best results for the MnSb terminated layer. Here nearly perfect spin polarization is observed on all atoms, except for the surface Mn. On this atom the polarization is almost completely lost. Note that experimentally a high spin polarization has only been observed recently (with spin-polarized inverse photoemission) by Ristoiu *et al.*[30] They studied several (100) surfaces, but only for one surface a high P was observed. That surface was probably terminated with a MnSb layer, i.e., similar to our calculated MnSb terminated surface. However, even for this experimentally favorable case we find a nonperfect polarization when probing with atomic scale resolution. In general practice the situation is even worse, as surface segregation is known to occur without special precaution.[15,31] Indeed, the surface for which Ristoiu *et al.* obtained a high spin polarization was metastable.[30]

The above findings make sense if we consider the rationale for the half metallicity of bulk NiMnSb.[5] The Mn and Sb atoms dominate the bandstructure near the Fermi level. They are tetrahedrally surrounded by Ni atoms, i.e., their local environment is similar to that in a zincblende semiconductor. As a consequence the minority spin bandstructure strongly resembles that of a typical zincblende semiconductor, like GaAs and many other III-V and II-VI materials, and therefore possesses a gap at the Fermi level. Thus the half metallicity is a direct consequence of the resemblance to the zincblende lattice. To destroy the gap it is enough to interchange the positions of Ni and either Mn or Sb. From this explanation it follows that any instance of symmetry breaking, like disorder,[32] a surface or an interface is *a priori* expected to result in a surface (interface) layer with incomplete spin polarization. Disorder is the least harmful, as it can be minimized by a better sample preparation. For surfaces and interfaces the problem is more fundamental. The latter are a crucial ingredient of any spin-electronic device.

Since in practical applications the interface is crucial, we tried to devise a cure, i.e., to make the interface half metallic by a judicious tuning of its composition and structure. We carried out calculations on several (111) and (100) interfaces with III-V and II-VI semiconductors. The similarity of the bandstructure to that of the NiMnSb minority spin-component motivated the choice for such materials. All attempts with (100) interfaces were fruitless. For (111) interfaces the constraints on coordination near the interface are less involved, and we had more hope to obtain a half-metallic interface. Indeed we did obtain one half-metallic NiMnSb/CdS interface (of several possible interface structures),[33,34] although with a somewhat unexpected interface geometry.

The supercell for the half-metallic interface is similar to that of the (111) NiMnSb/vacuum system described above. However, it has nine instead of six formula units of fcc NiMnSb and, instead of vacuum, nine units of CdS. The CdS stacking is: an S layer, a Cd layer, and two empty layers.[35] Atomic positions have been relaxed along [111] and the height of the cell has been optimized ($c=63.1$ Å). The local stability was checked with a few symmetry-breaking displacements in the ab plane. The cell necessarily contains two inequivalent interfaces, of which only one is half metallic. Layers have been numbered in a similar fashion as above, starting from 1 at the half-metallic interface and increasing when moving into both NiMnSb and CdS. Thus the interface is in between Sb^1 and S^1 (see Fig. 2).

Figure 3 shows the projected DOS' for the layers next to the half metallic interface (Sb^1-Mn^3, S^1-Cd^2) and for the central layers of the NiMnSb (Sb^{13}-Mn^{15}) and CdS (S^9-Cd^{10}) slabs. Notice that the bulk DOS is well reproduced in the central parts of the NiMnSb and CdS slabs. Moreover, at the half metallic interface the minority DOS vanishes at the Fermi level. The NiMnSb DOS is rather similar to its bulk. Remnants of the interface state at the other (not half-metallic) interface are negligibly small at the half-metallic interface. On the enlarged scale of the CdS partial DOS these remnants can just be discerned. The DOS has been calculated with a $9\times9\times1$ **k**-point mesh.[28]

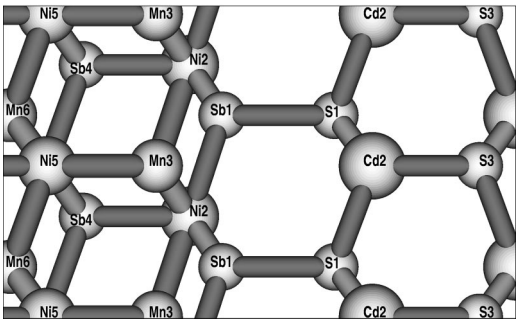

FIG. 2. Structure of the half metallic NiMnSb(111)/CdS(111) interface. The [111] axis runs horizontally, from left to right. Notice the Sb-S bond at the interface ($d_{Sb^1\text{-}S^1}=2.7$ Å).

Figure 2 depicts the structure of the half-metallic interface. Note the Sb-S bond (2.7 Å) at the interface. Both atoms in this bond are tetrahedrally coordinated, like in bulk NiMnSb and CdS. However, for Sb(S) one bond with a Ni(Cd) has been replaced with the S-Sb bond. The Sb-S bond is unexpected: a continuation of the alternation of cations and anions (as in both bulk materials) would seem most appropriate, but both Sb and S play the role of ''anion'' in, respectively, NiMnSb and CdS, i.e., they form an ''anion-anion'' bond. However, in the half-metal the concept of an ''ion'' is ill-defined since the screening is metallic. Moreover, we note that similar Sb-S bonds are present in the semiconducting minerals gudmundite (FeSbS),[36] costibite and paracostibite (CoSbS).[37] These minerals have a structure related to marcasite: the Sb and the S pair, forming Sb-S bonds with lengths of 2.61, 2.52, and 2.51 Å, respectively. The first coordination shell of Sb (S) contains one S (Sb) and three Fe or Co atoms. Thus the coordination and chemical bonding in these minerals, stable on a geological time scale, are analogous to that of the interface we obtain.

Summarizing, we have shown that stoichiometric, bulk-terminated NiMnSb (100) and (111) surfaces are not half metallic. Also NiMnSb/insulator interfaces are not half metallic in general. This breakdown of the half-metallic behavior arizes as a consequence of the symmetry breaking at the surface. In our opinion, this explains why experiments using surface and interface sensitive probes do not find 100% spin-polarization[7,13,15] for the charge-carriers. Alternatively, these experimental findings could be explained from disorder in NiMnSb. Disorder has been shown to spoil the half metallicity.[32] However, there is no direct experimental evidence available for disorder in NiMnSb, whereas surface segregation is well documented for NiMnSb.[30,31] Moreover, bulk-sensitive probes in general confirm the half-metallic behavior.[12,16–18] Therefore we consider this alternative explanation rather unlikely.

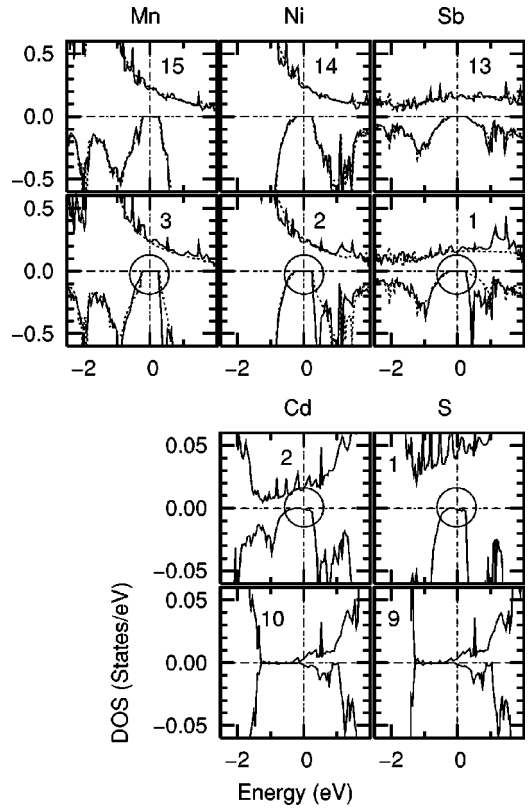

FIG. 3. Atom projected DOS of the slab with the half metallic NiMnSb(111)/CdS(111) interface. The projected DOS are only shown for the layers next to the half-metallic interface (Sb^1-Mn^3, S^1-Cd^2) and for the central layers of the NiMnSb (Sb^{13}-Mn^{15}). The Fermi level is at 0. Bulk DOS curves of NiMnSb have been added with dotted lines. The DOS has been calculated with the PAW method for Mn. Half metallicity is signalled by the vanishing DOS at the Fermi level. This is highlighted by a circle.

In order to successfully grow high-performance magnetoresistive tunnel junctions with NiMnSb, it is of paramount importance to restore the half metallicity at the interface. This can be achieved by a *suitable choice* of the interface, as we have shown here for a NiMnSb(111)/CdS(111) interface.[34,38] Thus spin-flip processes at the interface should be suppressed and electrons at the Fermi-energy can tunnel into the insulator material with 100% spin-polarization.

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[1] S. Bandyopadhyay, Phys. Rev. B **61**, 13 813 (2000).

[2] G. Schmidt, D. Ferrand, L. W. Molenkamp, A. T. Filip, and B. J. van Wees, Phys. Rev. B **62**, R4790 (2000).

[3] R. Fiederling *et al.*, Nature (London) **402**, 787 (1999).

[4] The proper definition of the spin polarization P depends on the experimental probe. See, e.g., I. I. Mazin, Phys. Rev. Lett. **83**, 1427 (1999). In half-metallic systems all definitions give $P=100\%$.

[5] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).
[6] K. Schwarz, J. Phys. F: Met. Phys. **16**, L211 (1986).
[7] R. J. Soulen, Jr. *et al.*, Science **282**, 85 (1998).
[8] W. E. Pickett and D. J. Singh, Phys. Rev. B **53**, 1146 (1996).
[9] P. K. de Boer, H. van Leuken, R. A. de Groot, T. Rojo, and G. E. Barberis, Solid State Commun. **102**, 621 (1997).
[10] J. H. Park *et al.*, Nature (London) **392**, 794 (1998).
[11] K. L. Kobayashi, T. Kimura, H. Saweda, K. Terakura, and Y. Tokura, Nature (London) **395**, 677 (1998).
[12] R. B. Helmholdt, R. A. de Groot, F. M. Mueller, G. P. van Engen, and K. H. J. Buschow, J. Magn. Magn. Mater. **43**, 249 (1984).
[13] C. T. Tanaka, J. Nowak, and J. S. Moodera, J. Appl. Phys. **86**, 6239 (1999).
[14] J.-P. Schlomka, M. Tolan, and W. Press, Appl. Phys. Lett. **76**, 2005 (2000).
[15] G. L. Bona, F. Meier, M. Taborelli, E. Bucher, and P. H. Schmidt, Solid State Commun. **56**, 391 (1985).
[16] K. E. H. M. Hanssen, P. E. Mijnarends, L. P. L. M. Rabou, and K. H. J. Buschow, Phys. Rev. B **42**, 1533 (1990).
[17] F. B. Mancoff, B. M. Clemens, E. J. Singley, and D. N. Basov, Phys. Rev. B **60**, R12 565 (1999).
[18] M. J. Otto *et al.*, J. Phys.: Condens. Matter **1**, 2351 (1989).
[19] J. P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).
[20] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[21] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[22] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[23] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).
[24] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[25] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14 251 (1994).
[26] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[27] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[28] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).
[29] P.E. Blöchl, O. Jepsen, and O.K. Andersen, Phys. Rev. B **49**, 16 223 (1994).
[30] D. Ristoiu *et al.*, Europhys. Lett. **49**, 624 (2000).
[31] D. Ristoiu, J. P. Nozières, C. N. Borca, B. Borca, and P. A. Dowben, Appl. Phys. Lett. **76**, 2349 (2000).
[32] D. Orgassa, H. Fujiwara, T. C. Schulthess, and W. H. Butler, Phys. Rev. B **60**, 13 237 (1999).
[33] Note that, with a 2% discrepancy, CdS matches the NiMnSb lattice reasonably well.
[34] All other (111) interfaces that we tried were not half metallic, except for a NiMnSb/InP interface with very similar geometry and an Sb-P bond. InP might be a better material for applications, because the lattice mismatch with NiMnSb is only 1%.
[35] For the insulator CdS we used both the zincblende (fcc) and wurtzite stacking (hcp), in order to obtain two reasonable interfaces within the constraint of periodic repetition.
[36] M. J. Buerger, Z. Kristallogr. Kristallgeom. Krystallphys. Kristallchem. **101**, 290 (1939).
[37] J. F. Rowland, E. J. Gabe, and S. R. Hall, Can. Mineral. **13**, 188 (1975).
[38] We note that much experience exists with the self-organized growth of CdS nanocrystals [e.g., H. Bekele, J. H. Fendler, and J. W. Kelly, J. Am. Chem. Soc. **121**, 7266 (1999)], opening avenues towards the construction of a self-assembling quantum computer proposed in Ref. 1.